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Novel membrane mimetic systems based on amphiphilic oxyethylated calix[4]arene: Aggregative and liquid crystalline behavior

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ABSTRACT

Self-organization of amphiphilic calixarenes oxyethylated at a lower rim has been investigated in water and water–organic solutions. In the range of isotropic solutions three types of structural transitions were indicated by a complex of methods. The first critical point indicated by surface tension, dynamic light scattering and atomic force microscopy methods is probably connected with the formation of "infinite" organized structures (of hundreds nanometers in size) through the open association model. This aggregative phenomenon covers the concentration range below 10^{-3} M. In the case of aqueous calixarene solutions these large aggregates co-exist with small micelle-like particles and undergo a rearrangement with an increase in the concentration. The second structural transition occurs beyond 10^{-3} M. It is revealed in aqueous calixarene solutions by surface tension, spine probe, viscosimetry and dynamic light scattering methods. Small aggregates (~10 nm in diameter) are formed in this range through a closed model typical for conventional surfactants. The third transition indicated by viscosimetry and in single case by tensiometry can be connected with an elongation of aggregates. The polarization microscopy and X-ray diffraction studies reveal the anisotropic behavior with the concentration of solutions. Parameters of the existence of liquid crystalline mesophases are found to be influenced by the structure of substituents at both the upper and lower rims, as well as by the nature of solvent.

It is generally recognized that self-organizing systems based on synthetic amphiphilic compounds due to their relative simplicity make it possible to isolate single factors and obtain information on the structural behavior of their prototypes, i.e. natural organized systems, in particular biomembranes [1]. This approach is considered to be a biomimetic way based on the analogy between synthetic and natural amphiphiles. Both exhibit the capacity to form aggregates of different morphology and to interact selectively and reversibly with a diversity of organic and bioorganic guests, thereby controlling their physico-chemical properties. The topic of high importance is that biological amphiphiles and drugs are capable of forming various types of aggregates differing in their size, packing mode, morphology and hence in their functionality. The structural diversity of biosystems is mostly due to the contribution of various non-covalent interactions including van der Waals forces, hydrogen bonds, hydrophobic and stacking effects, etc. Another essential feature is their capacity to associate through different mechanisms. According to Ref. [2] two models of association are typical for amphiphiles depending on their geometry and hydrophilic–lipophilic balance. In particular, the closed packing mode is observed for conventional surfactants with distinctly separated hydrophilic and hydrophobic fragments, while an alternative open model is observed for bio-relevant amphiphiles including drugs. The former usually results in the formation of small micelle-like aggregates with a marked surface curvature, while the latter leads to the formation of "infinite" structures of large size with a small, if any, surface curvature. Such a structural lability of biospecies makes it possible for them to adjust to the microenvironment and participate in metabolic transformations. Structural transitions are known to play a key role in the functioning of biomembranes, in particular, in the transport through lipid bilayers, with the fusion/fission processes involved. For example,

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